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Structure and activity relationships for CO_2 regeneration from aqueous amine-based absorbents

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ABSTRACT

A study to determine the relationships between structure and activity of various amine-based CO_2 solvents was performed. The desorption of CO_2 from saturated solvents at 80 °C and atmospheric pressure was measured to assess the initial desorption rate and desorption capacities at pseudo-equilibrium. Evaluation of the desorption capacity at lower temperature, 80 °C, will give a better understanding for more energy efficient and lower circulation rate absorbent for CO_2 absorption process. Results showed that an increase in chain length between the amine and different functional groups in the solvent structure up to four carbon, results in an increase in initial desorption rate and also an increase in the desorption capacity at pseudo-equilibrium was observed for most solvents. Steric hindrance effect was noticed when a side chain with an alkyl group was present at α-carbon position to amine group in the structure. Increase in the number of the amine group in solvent structure, results in higher desorption capacity up to 75% of CO_2 is desorbed. Aromatic amines substituted with an amine group by a side chain at the cyclic ring shows an increase in desorption capacity at pseudo-equilibrium compare to other group substitution.

Keywords: Desorption; CO_2; Amine; Acid gases; Regeneration; Absorbent

1. Introduction

Although the absorption of acid gases such as CO_2 in aqueous amine solutions, like e.g. monoethanolamine (MEA) from natural gas seems proven technology, removal of CO_2 from flue gases is not as straightforward as it could be expected. In these currently used systems a major part of the operational costs is caused by the solvent regeneration (up to 40%). In industrial processes, high temperatures (>100 °C) are used to regenerate MEA solutions. Usually high-pressure steam is applied, which provides the heat of reaction and enables the transport of CO_2 out of the reactor. The regeneration process is usually done at temperatures in excess of the boiling temperature, as the chemical kinetics of regeneration increases with temperature. The energy consumption in the stripper reboiler is estimated to be 15–30% of the net power production of a coal-fired power plant for about 90% CO_2 removed. The development of improved solvents with lower regeneration energy requirement can therefore be identified as the highest priority research and development objective for amine-based CO_2 capture systems. Such improvements are needed to reduce the too high-energy consumption of current systems, which is the major contributor to the relatively high cost of this technology.

A complete and rigorous (rate-based) simulation model of chemical absorption–desorption process requires a large number of physico-chemical data (solvent viscosity, density, diffusivities, kinetics data, and equilibrium model). Moreover to characterize a large number of solvent systems with all this information is a tedious task and could not be performed for a few solvents in a short time. Also studies devoted to desorption are not as numerous as those concerning absorption. More specifically, the relationship of structure and regeneration characteristics of various amines-based absorbent for CO_2 is hardly studied. Therefore, a screening method has been developed for the desorption of CO_2 from various loaded amine-based aqueous absorbents. The main aim in this investigation is to perform the screening of various solvents on their regeneration behaviour at low temperature and atmospheric pressure, with respect to rapid regeneration rate and low evaporation solvents losses especially. Desorption of CO_2

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from various amine-based absorbents was measured to assess the amount of CO_2 desorbed and the overall rate of desorption at 80 °C. In this study the effects which were investigated are the chain length, number of functional groups, different functional groups substitution at the α-carbon to the amines group, cyclic amine, substituted cyclic amines, etc. compared the performance of MEA which acts as a base case. Based on these results a better understanding of the structural effect on CO_2 desorption will be developed. This study will be advantageous in the development of an improved efficiency amine-based CO_2 absorbent.

2. Experiment

The various amine-based absorbents were tested in a simple screening apparatus (see Fig. 1), in which relative rates of the desorption and desorption capacity at pseudo-equilibrium can be measured and compared to the MEA default case. Due to the selection of the lower temperature of 80 °C for these experiments, compared to the commercial process regeneration temperatures of 120 °C, complete equilibrium for these desorption experiments was difficult to achieve. For these desorption experiments pseudo-equilibrium in this study work was defined for which most of the absorbents were close to their equilibrium composition. As desorption of CO_2 is faster compared to the absorption process, a desorption time of 20 min was found to be sufficient for the evaluation. The apparatus was designed to operate at atmospheric pressure and temperatures up to 80 °C. In a typical experiment first the solvent was degassed for sufficient time (approximately 2 h) and then saturated with pure CO_2 for approximately 1 h. This saturation of solvent was performed at 30 °C temperature and at atmospheric pressure. Once the solvent is completely saturated, a sample is taken to determine the total CO_2 loading in the solvent by a desorption/titration procedure as described by Blauwhoff et al. (1984). Once the total CO_2 loading is determined the known volume of a saturated amine sample of 40 ml is taken from the absorption column and is transferred into the desorption vessel. The temperature inside desorption vessel was maintained at 80 ± 0.5 °C. To ensure that the temperature in the absorbent solution during desorption remained constant, the solution is stirred continuously with a constant speed in every experiment. Saturated absorbent solution reached 80 °C within approximate 2.5 min.

The carbon dioxide released during this heating time is measured by a gas burette connected to the desorption vessel. When the solvent temperature is 80 °C the valve of the gas burette is closed and the CO_2 is monitored by online CO_2 IR detector. At the same time pure N_2 gas is bubbled through the saturated absorbent to increase the interfacial area for CO_2 desorption. The vapour leaving the desorption vessel containing the CO_2 and N_2 is fed into a vertical condenser. The condenser was kept at a temperature of 20 °C. The gas leaving the top of the condenser was at 25 ± 1 °C and thus contained only about 3 vol.% of water vapour. Further in this outlet stream, N_2 gas is added for dilution. This diluted stream is passed through an ice trap with a temperature of approximately 2 °C to remove the remaining amount of water vapour from the stream.

Next this stream is send to CO_2 IR detector where the amount of CO_2 in the stream is measured. To ensure that there was no significant depletion on the partial pressure of CO_2 during desorption experiment, the flow of N_2 gas is kept very low in the saturated absorbent. Hence the effect on CO_2 partial pressure was negligible in the desorption experiment. Therefore, the complete desorption experiment was at prevailing atmospheric pressure, as the pressure-drop during the experiment was very small. The N_2 gas flow in solvent and for dilution was kept constant in every experiment. After a certain time in this desorption experiment, when pseudo-equilibrium is reached, the total CO_2 loading in the desorbed solvent is determined by desorption/titration procedure as described by Blauwhoff et al. (1984). The time for each desorption experiment is kept constant. The amine concentration in the solution could vary with the type of compound only to, e.g. molecular weight and solubility. As a base case MEA absorbent 2.5 moles/l concentration was chosen for comparison.

3. Results and discussion

Examination of the desorption behaviour from a saturated amine-based solvent with pure CO_2, allows for a comparison of the initial desorption rates and desorption capacity defined as the amount of CO_2 that remains in the solvent at the experimental conditions at the end of the experiment. From the initial desorption rate, an indication can be obtained about the reactivity of the various amine-based absorbents investigated. It must be noted, however, that due to mass transfer effects,

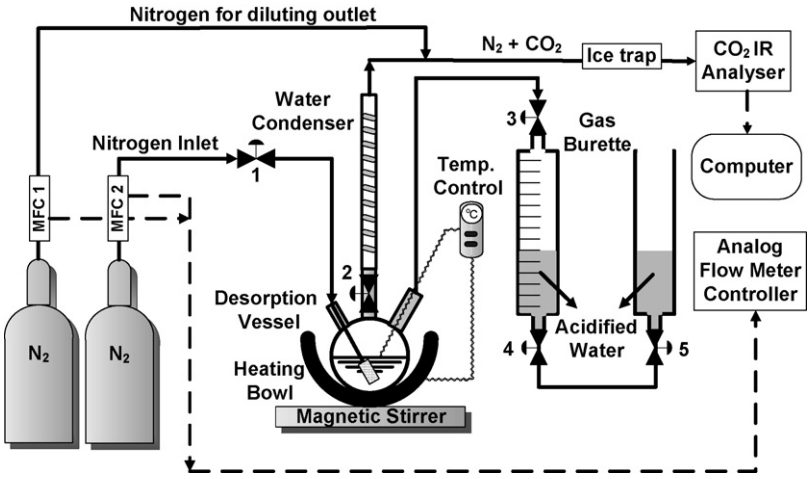


Fig. 1 – Schematic diagram of the experimental set-up for determining the desorption capacity of various amine-based absorbents.

e.g. interfacial area and enhancement factor that are contactor specific, no quantitative conclusions can be presented beforehand. However, the stirring speed during the experiment was the same for all solvent that were investigated, so the differences that would arise are mainly due to the variations in physical properties, like e.g. interfacial tension, density, viscosity and heat of absorption and these are characteristics for each solvent combination. The solvents with the lower desorption capacities are more suitable as they will decrease the solvent circulation rate in the CO_2 capture process. Hence, that will be economically beneficial for the whole CO_2 absorption process. Also the evaluation of the desorption rate at 80 °C will give the indication of energy efficiency of the solvent that might result in a decrease in energy cost for the CO_2 absorption process. All experiments were repeated three times for each absorbent and the experimental deviation (based on propagation of error) was estimated to be approximate 4%.

3.1. *Effect of chain length in alkanolamine*

In Fig. 2(a and b) and Table 1, the effect of an increase in the chain length between the amine and hydroxyl group on the desorption rate and capacity of alkanolamine-based absorbents is shown.

In these experiments the chain length varied from a two carbon chain (MEA) up to five (5-amino-1-pentanol), respectively. Fig. 2(a) shows the result overview of the complete desorption experiments of CO_2 from aq. MEA, which is regarded as a base case. As it can be seen from Fig. 2(a) in the beginning of the experiment from time 0 to 2.5 min, the desorption rate is influenced by the increasing temperature which is starting from 30 °C up to 80 °C. The desorption rate is increasing with temperature. Hence, in this region the desorption is affected by combination of phenomena; lower physical solubility, changing thermodynamics and increasing kinetics with temperature. It is clear that neither qualitative nor quantitative conclusions can be presented during this period of experiments. Once the temperature of the absorbent solution is reached 80 °C, the desorption rate would be more effected by chemical desorption. Therefore, the evaluation of the initial desorption rate was done once the temperature in the absorbent was reached at 80 °C and remained constant. It should be noticed however that the slope of the initial desorption rate was taken from the CO_2 concentration in moles/m^3 s unit. Due to the lower concentration of some absorbents, which results in the lower concentration of CO_2 in moles/m^3. Hence, this might result in lower slope values of the initial desorption rate in some absorbents.

In Fig. 2(b), the overall results are presented. It must be noticed that the concentration of all alkanolamine was kept

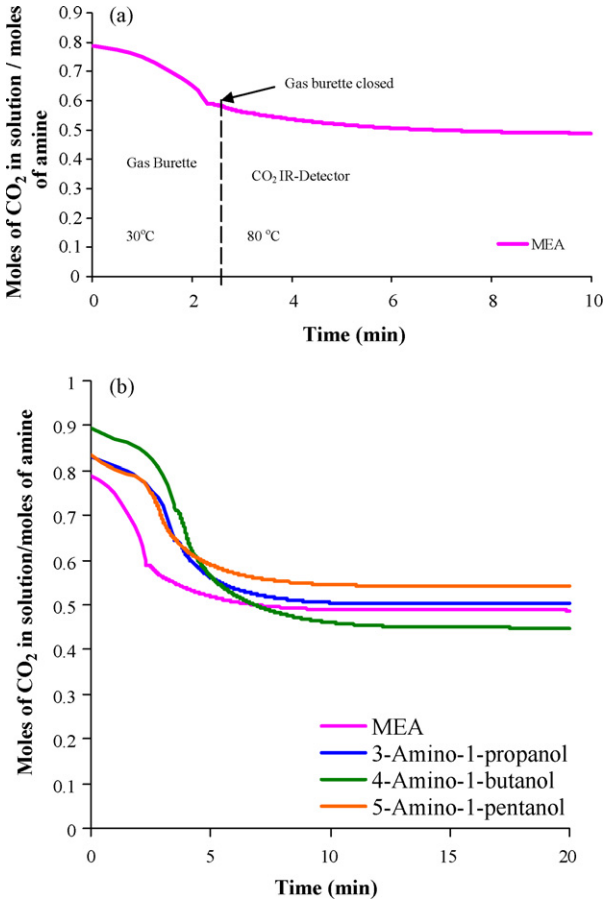


Fig. 2 – (a) Detailed overview on desorption of CO_2 from aq. MEA. (b) Influence of the chain length in aq. alkanolamine-based absorbent for desorption of CO_2.

to 2.5 moles/l. For MEA the carbamate is the main product in CO_2 absorption, while bicarbonate and carbonate are present in very small quantities. The high loading in MEA of 0.79 moles of CO_2/moles of amine occurred due to the conversion of the carbamate to bicarbonate and hence results in an increase in mole fraction of CO_2 that is a result of physical absorption. The MEA absorption loading is in comparison with the results presented in literature Shen and Ll (1992). The effect of an increase in chain length on the initial desorption rate for alkanolamine is clearly shown in Fig. 2(b).

It can be noticed that for chain lengths up to 4 carbon (4-amino-1-butanol) (see Table 1) an increase in initial desorption rate observed. Further increase in chain length decreases the initial desorption rate. At this stage no further qualitative analysis will be presented on the initial desorption rate. As the desorption rate is a complex interaction between mass

Table 1 – Capacity of aq. alkanolamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
H_2N OH Monoethanolamine	0.79	0.49	2.61E−2
H_2N OH 3-Amino-1-propanol	0.83	0.45	5.96E−2
H_2N OH 4-Amino-1-butanol	0.89	0.44	1.02E−1
H_2N OH 5-Amino-1-pentanol	0.83	0.54	4.08E−2

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

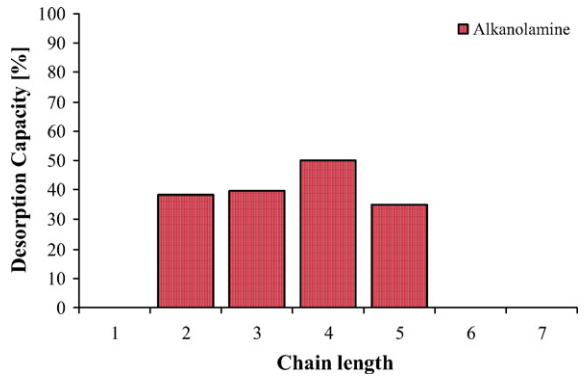


Fig. 3 – Influence of the chain length in aq. alkanolamine-based absorbents on desorption capacity (%) of CO_2 at pseudo-equilibrium.

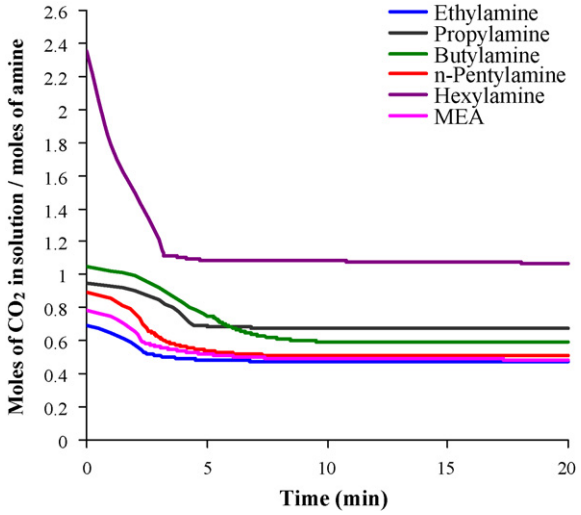


Fig. 4 – Influence of the chain length in aq. alkylamine-based absorbent for desorption of CO_2.

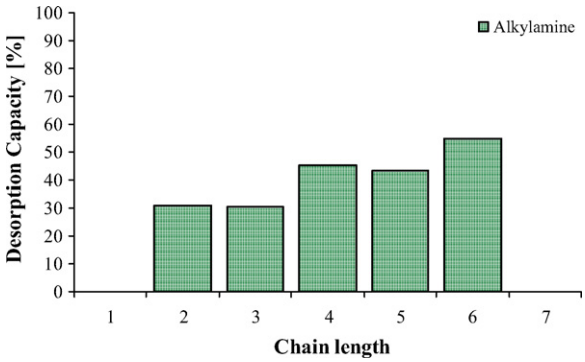


Fig. 5 – Influence of the chain length in aq. alkanolamine-based absorbents on desorption capacity (%) of CO_2 at pseudo-equilibrium.

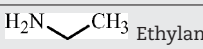
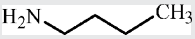
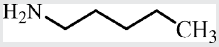
transfer, kinetics and equilibrium. The interpretation is not as straightforward as was expected before hand. Increase in the chain length results in a slight increase in CO_2 desorption capacity till four carbon up to 0.44 moles of CO_2/moles of amine that is approximate 49% of CO_2 is desorbed (see Fig. 3 and Table 1). Further increase in chain length results in a decrease in desorption capacity. Hence, overall in alkanolamine desorption capacity increases only up to four carbon chain length as well as the initial desorption rate.

3.2. *Effect of chain length in alkylamines*

In the experiments with alkylamine-based solvents the chain length varied from two carbon chain (ethylamine) up to six (hexylamine) respectively in their chemical structure. In Fig. 4, the overall results are presented. It must be noticed that the concentration of the alkylamine up to the five carbon chain (*N*-pentylamine) was kept to 2.5 moles/l. Due to the low solubility in water the concentration of six carbon chain (hexylamine) was only 0.1 moles/l. The influence of the chain length in alkylamines is shown in Figs. 4 and 5 and Table 2. Result shows that the initial desorption rate in alkyl amine increases gradually with an increase in chain length up to four carbon. Interestingly, the six carbon chain length absorbent (hexylamine) was found to be having very fast desorption rate in the heating up period, as the most of the CO_2 is desorbed until the temperature of 80 °C is reached. However, the value of the initial slope, i.e. the desorption rate, is low (see Table 2) that could be due to the lower concentration of hexylamine solution being used in the experiment. Hence, that results in a lower concentration of CO_2 present in the absorbent in moles/m^3 s unit. Still when comparing to the initial desorption rate from Fig. 4 in hexylamine in CO_2 is fast with respect to the other alkylamine.

There can be two possible explanations presented for this behaviour, either the stability of the hexylamine carbamate is very low, or there is hardly any formation of the carbamate in the solution which results into a substantially higher concentration of bicarbonate and hence, generate faster CO_2 release during desorption. From Fig. 5 and Table 2, results shows that an increase in the chain length from a two carbon chain (ethylamine) to a three carbon chain (propylamine) the CO_2 desorption capacity remains the same that is 30% of CO_2 is

Table 2 – Capacity of aq. alkylamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 Ethylamine	0.69	0.48	2.94E−2
 Propylamine	0.97	0.68	1.46E−1
 Butylamine	1.07	0.59	1.44E−1
 *N*-pentylamine	0.90	0.51	3.16E−2
 Hexylamine	2.36	1.07	2.45E−2

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

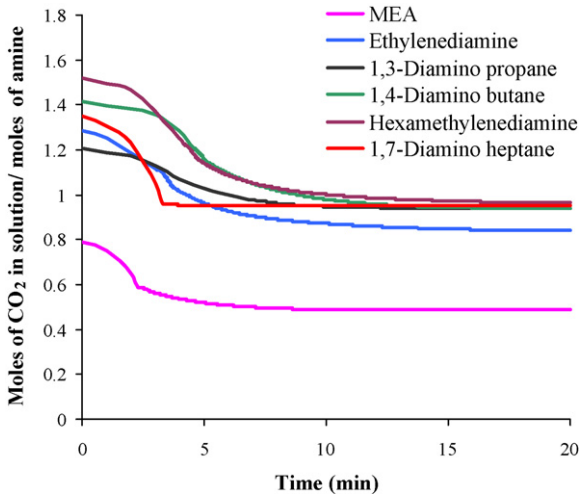


Fig. 6 – Influence of the chain length in aq. diamine-based absorbent for desorption of CO_2.

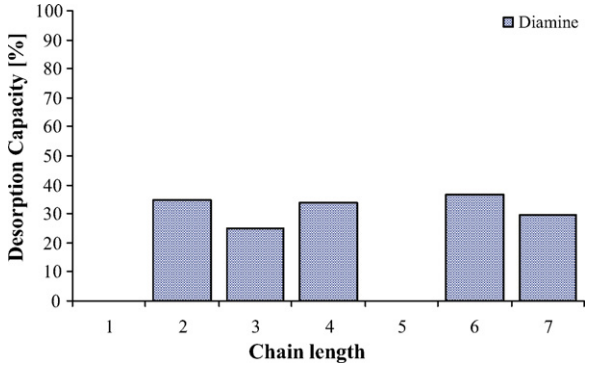


Fig. 7 – Influence of the chain length in aq. diamine on desorption capacity (%) of CO_2 at pseudo-equilibrium.

desorbed. Further increase in the chain length results in higher desorption capacity as in four carbon chain (butylamine) in which 45% of CO_2 is desorbed. Whereas, with a six carbon chain length (hexylamine) desorption capacity reaches up to 1.07 moles of CO_2/moles of amine that is 54% CO_2 is desorbed.

3.3. *Effect of chain length in diamines solvents*

In the diamine-based absorbent experiments the chain length was varied from two carbon chain (ethylenediamine) up to seven (1,7-diaminoheptane), respectively. In Fig. 6 the overall results are presented. It must be noticed that the concentration of diamine up to six carbon chain (hexadimethylenediamine) was kept to 2.5 moles/l. Due to the low solubility in water the concentration of the seven carbon chain length absorbent (1,7-diaminoheptane) was kept at 1.5 moles/l. Figs. 6 and 7 and Table 3, show that an increase in chain length decreases the initial desorption rate in diamines up to three carbon chain length (1,3-diaminopropane).

However, further increase in chain length from four (1,4-diaminobutane) up to six carbon (hexadimethylenediamine) results in an increase in initial desorption rate (see Table 3). Higher chain length with seven carbon results in a decreased initial desorption rate (1,7-diaminoheptane). Hence, from these results it can be noticed that the ethylenediamine and hexadimethylenediamine could thus have a greater potential for CO_2 desorption as they have showed the higher initial desorption rate (Singh et al., 2007).

An increase in the chain length in diamine-based absorbent results in an increase in the desorption capacity as can be noticed in hexadimethylenediamine is up to 0.95 moles CO_2/moles diamine that is approximate 36% of CO_2 is desorbed (see Fig. 7 and Table 3). This might be caused by the effect from a decrease in stability of the carbamate with an increase in the chain length (Caplow, 1968). Therefore, the bicarbonate concentration is higher and hence, higher amount of CO_2 is released.

An interesting comparison could also be made on the effect of an increase in chain length in alkanolamine, alkylamine and diamine from Figs. 3, 5 and 7. It can be noticed that in alkanolamine desorption capacity is increased up to more than 50% of CO_2 is desorbed, when chain length is increased up to 4 carbon (4-amino-1-butanol). Whereas in alkylamines the CO_2 desorption capacity is highest with six carbon chain length (hexylamine) up to 50% of CO_2 is desorbed. In diamine-based absorbents there is a slight increase in desorption capacity up to six carbon chain length (hexadimethylenediamine) with a desorption capacity of around 40% CO_2 is desorbed. Overall comparison shows that the alkanolamine with a four carbon chain length and alkylamine with six carbon chain length has the highest CO_2 desorption capacity. Therefore, from these results it is clear that the structural effect is important in the behaviour of amine-based absorbents for CO_2 desorption.

3.4. *Effect of side chain*

The position of the different functional groups in the structure of various amine-based absorbents is an important factor (Chakraborty et al., 1986, 1988).

Table 3 – Capacity of aq. diamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
H_2N NH_2 Ethylenediamine	1.28	0.84	8.51E−2
H_2N NH_2 1,3-Diamino propane	1.27	0.94	5.38E−2
H_2N NH_2 1,4-Diaminobutane	1.42	0.94	9.20E−2
H_2N NH_2 Hexadimethylenediamine	1.52	0.95	9.66E−2
H_2N NH_2 1,7-Diaminoheptane	1.35	0.95	6.80E−3

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

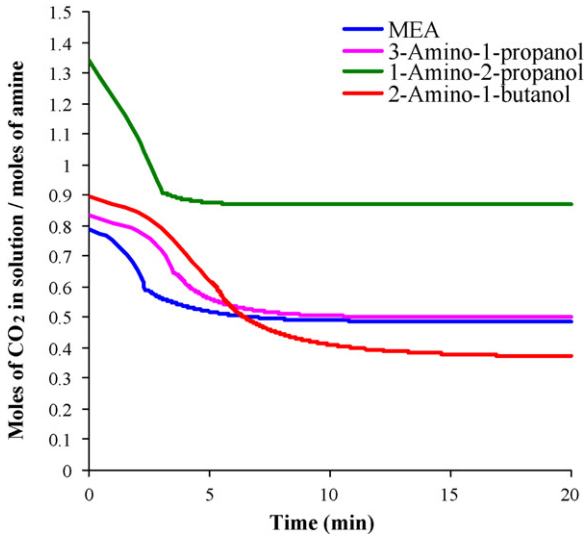


Fig. 8 – Influence of the hydroxyl group position in aq. alkanolamine-based absorbent for desorption of CO_2.

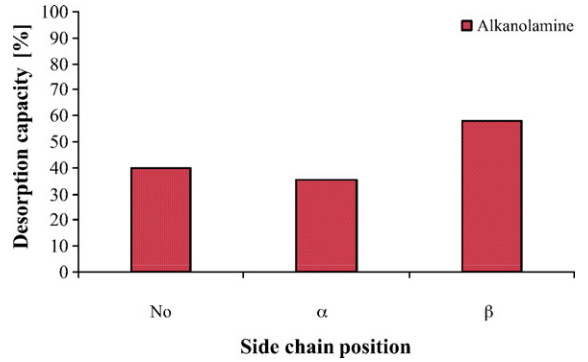


Fig. 9 – Influence of the hydroxyl group position in aq. alkanolamine on desorption capacity (%) of CO_2 at pseudo-equilibrium.

In Figs. 8 and 9 and Table 4 the effect of the position of substituted hydroxyl group is compared. It should be noticed that the concentration for 3-amino-1-propanol, and 2-amino 1-butanol was kept at 2.5 moles/l, whereas concentration used for 1-amino 2-propanol was 0.5 moles/l. In these experiments the hydroxyl group is positioned at α-carbon (2-amino 1-butanol) and β-carbon (1-amino 2-propanol) to the amine group in the absorbent structure is investigated. Fig. 8, shows that the hydroxyl group substitution on α-carbon (2-amino-1-butanol) to the amine group result in an increase of an initial desorption rate compared to the hydroxyl group substitution on β-carbon (1-amino 2-propanol) (see Table 4). These

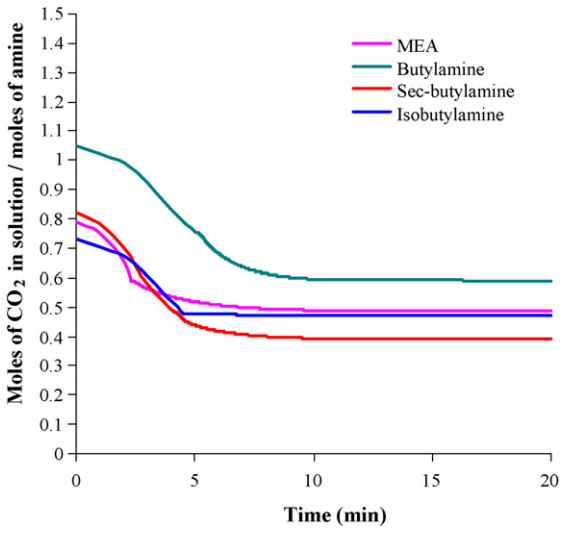
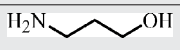
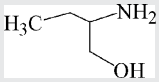
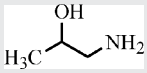


Fig. 10 – Influence of a methyl group position in aq. alkylamine-based absorbent for desorption of CO_2.

results explain the effect of steric hindrance caused at the amine group. At this stage no further qualitative analysis will be presented on the initial desorption rate. Desorption rate is a complex interaction between mass transfer, kinetics and equilibrium. Therefore, the interpretation is not as straightforward as was expected before hand. From Figs. 8 and 9 it must be noticed that a substitution of a hydroxyl group on the β-carbon (1-amino-2-propanol) to the amine group increases the desorption capacity up to 0.37 moles CO_2/moles amine, that means that approximate 58% of CO_2 is desorbed compared to the hydroxyl group substitution on α-carbon (2-amino-1-butanol) which has desorption capacity of 0.86 moles CO_2/moles amine (see Table 4) means 35% of CO_2 is desorbed. It is clear from these results that the hydroxyl group substitution at β-carbon (1-amino 2-propanol) to the amine group shows an increase in desorption capacity.

Furthermore, the effect of methyl group substitution at α or β-carbon to the amine group in alkylamine was also investigated (see Figs. 10 and 11 and Table 5). The concentration of butylamine, sec-butylamine and isobutylamine used in these experiments was 2.5 moles/l. Fig. 10, shows the effect of alkyl group substitution on the initial desorption rate. Results show that the alkyl group substitution on α-carbon (sec-butylamine) to amine group is having a higher initial desorption rate when compared to the alkyl group substitution at β-carbon to amine group (isobutylamine). The higher initial desorption rate in sec-butylamine might be caused by the effect of steric hinderance at the amine group that causes the faster breaking of

Table 4 – Capacity of aq. alkanolamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 3-Amino-1-propanol	0.83	0.50	5.96E−2
 2-Amino-1-butanol	1.34	0.86	1.35E−1
 1-Amino-2-propanol	0.89	0.37	5.30E−2

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

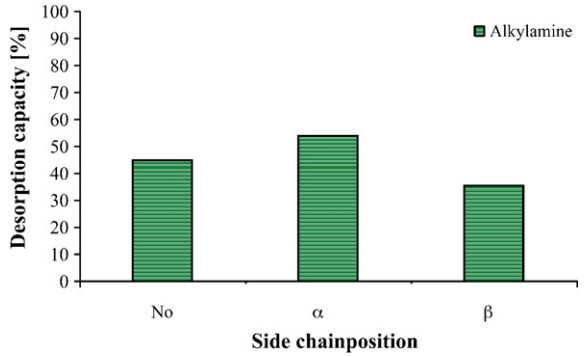


Fig. 11 – Influence of the alkyl group position in aq. alkylamine on desorption capacity (%) of CO_2 at pseudo-equilibrium.

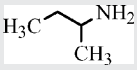
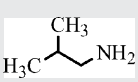
the C–N bond and results in an increases of the initial desorption rate. Figs. 10 and 11 show the overall results from alkyl-substituted absorbents. It can be noticed that the substitution of alkyl group at α-carbon (sec-butylamine) to amine group increases the desorption capacity up to 0.39 moles CO_2/moles, compared with alkyl group substitution on β carbon to amine group (isobutylamine) which has a desorption loading of 0.47 moles CO_2/moles amine (see Table 5) means 35% of CO_2 is desorbed (see Fig. 11).

This effect might be due to the fact that the alkyl group substitution at the α-carbon to the amine group creates steric hindrance at the reaction site and thus lowers the stability of the carbamate (Hook, 1997; Sartori and Savage, 1983). Which can cause enhanced hydrolysis of carbamate and hence, driving equilibrium towards bicarbonate. Therefore, higher concentration of bicarbonates are present in the system which results higher rate of CO_2 release during desorption.

Influence of amine group substitution by side chain in diamine-based absorbents is also investigated. Fig. 12 shows the overall desorption results. It should be noticed that the concentration of 1,2-diamino propane and 1,3-diamino propane was kept at 2.5 moles/l. The results from Fig. 12 shows that there is a slight decrease in an initial desorption rate when amine group is substituted at the β-carbon to amine group (1,2-diamino propane) in structure (see Table 6).

From Figs. 12 and 13 it can be concluded that the amine group substitution at the β-carbon to amine group (1,2-diamino propane) in the structure cause an increase in desorption capacity up to 0.74 moles CO_2/moles amine that is approximate 33% CO_2 is desorbed when compared to the nonsubstituted (1,3-diamino propane) with desorption capacity of 0.91 moles CO_2/moles amine (see Table 6) that is only 25% CO_2 is desorbed. Hence, amine group substitution on β-carbon to amine group by side chain in the structure results in an increase in desorption capacity whereas desorption rate is slightly decreased.

Table 5 – Capacity of aq. alkylamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 Butylamine	1.07	0.59	1.44E−1
 Sec-butylamine	0.85	0.39	1.04E−1
 Isobutylamine	0.73	0.47	1.90E−3

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

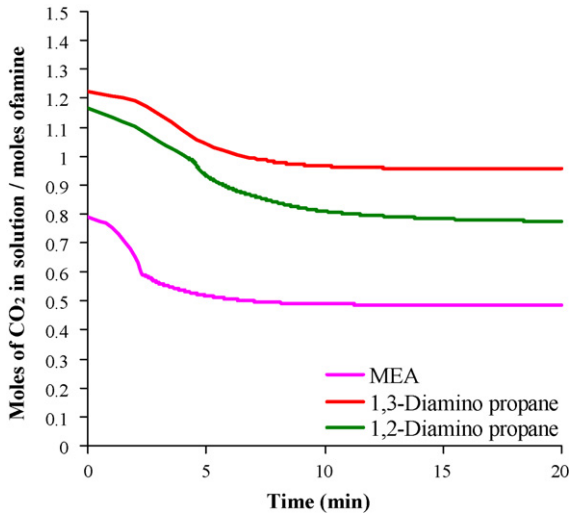
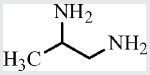


Fig. 12 – Influence of amine group position in aq. diamine-based absorbent for desorption of CO_2.

Table 6 – Capacity of aq. diamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 1,3-Diamino propane	1.27	0.91	5.38E−2
 1,2-Diamino propane	1.16	0.74	9.54E−3

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

When comparing the results from Figs. 9, 11 and 13 to investigate the effect of position of the various functional groups by side chain in amine-based absorbents. It can be noticed from these results that substitution of an alkyl group with the side chain at α-carbon to the amine group in structure results in an increase in desorption capacity. For alkanolamine and diamine substitution of a hydroxyl and amine group respectively by side chain at the β-carbon to amine group results in

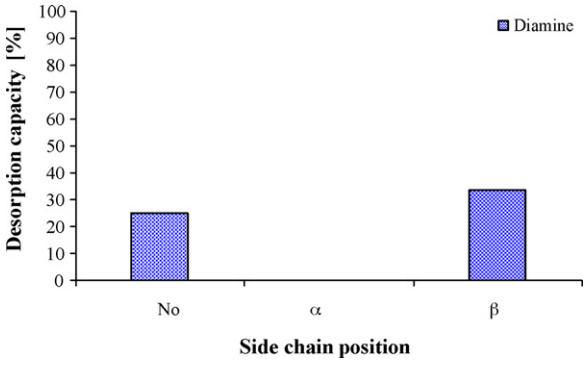


Fig. 13 – Influence of the amine group position in aq. diamine on desorption capacity (%) of CO_2 at pseudo-equilibrium.

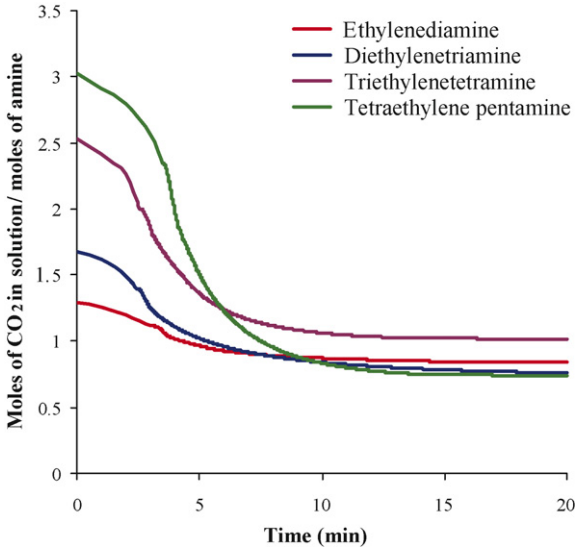


Fig. 14 – Influence of the number of amine groups in aq. amine-based absorbent for desorption of CO_2.

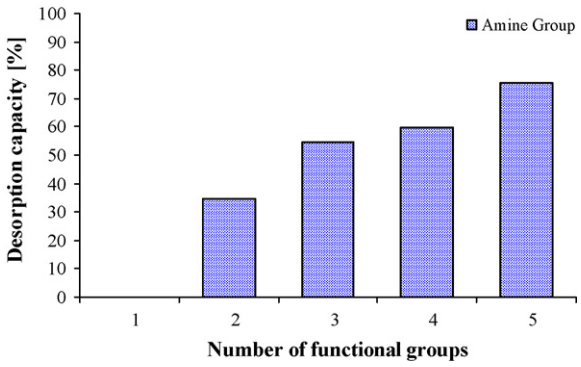


Fig. 15 – Influence of the number of amine groups in aq. amine based for the desorption capacity (%) of CO_2 at pseudo-equilibrium.

an increase in desorption capacity. However hydroxyl group substitution at the β-carbon to amine group (2-amino 1-butanol), is having highest desorption capacity around 60% of CO_2 is desorbed.

3.5. *Effect of number of functional groups*

The effect of an increase in the number of amine groups in the absorbent structure was investigated. It should be noticed that the concentration of ethylenediamine, diethylenetriamine and trietheylenetetramine was kept at 2.5 moles/l. Whereas due to high viscosity of tetraethylenepentamine, the concentration used for this absorbent was 0.5 moles/l. Figs. 14 and 15 and Table 7, show the effect of an increase in the number of amine group in the absorbent structure. Results from Fig. 14 shows that an increase in the number of amine groups increases the initial desorption rate (see Table 7). This might be caused by an increase in number of amine group creates more reaction sites available for the reaction with CO_2.

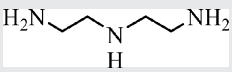
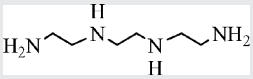
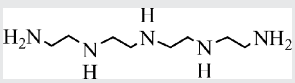
Therefore, more CO_2 could be present in bicarbonate form and increases in faster release of CO_2 in desorption. Still when compared to the initial desorption rate of four and five amine groups in the structure there is no further enhancement of the initial desorption rate.

Results from Figs. 14 and 15 show that an increase in number of amine groups from 2 (ethylenediamine) up to 5 (tetraethylenepentamine) shows an increase in desorption capacity. In tetraethylenepentamine the desorption capacity reaches about 0.74 moles CO_2/moles amine means is approximate 75% of CO_2 is desorbed. Hence, a higher number of amine groups present in the absorbent structure results in an increase in desorption capacity.

The effect of an increase in number of the hydroxyl group was also investigated. It should be noticed that the concentration of *N*-(2-hydroxyethyl)ethylenediamine and *N*,*N*′-bis (2-hydroxyethyl)ethylenediamine) is kept at 2.5 moles/l. Results from a diamine-based alkanolamine absorbent with one (*N*-(2-hydroxyethyl)ethylenediamine) and two hydroxyl groups (*N*,*N*′-bis(2-hydroxyethyl)ethylenediamine) is presented in Figs. 16 and 17 and Table 8. When comparing the initial desorption rate of one and two hydroxyl group diamine absorbents to the solvent with two hydroxyl groups present in the structure shows that it is having slightly higher initial desorption rate. This increase in initial desorption rate could be caused by the effect of steric hinderance at the reaction site that is created by hydroxyl group which results in faster release of CO_2.

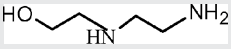
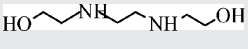
Fig. 17 shows that the increase in the number of hydroxyl groups in the diamine absorbent increases the desorption capacity as for (*N*,*N*′-bis(2-hydroxyethyl)ethylenediamine) the desorption loading is 0.41 moles CO_2/moles amine that means approximate by 66% of CO_2 is desorbed. This might be caused by the presence of steric hindrance effect around both amine group when two hydroxyl groups are present (*N*,*N*′-bis(2-

Table 7 – Capacity of aq. amine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 Ethylenediamine	1.08	0.84	8.51E−2
 Diethylenetriamine	1.83	0.76	1.54E−1
 Triethylenetetramine	2.51	1.02	3.67E−1
 Tetraethylenepentamine	3.03	0.74	3.18E−1

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

Table 8 – Capacity of aq. diamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 N-(2-Hydroxyethyl)ethylenediamine	1.36	0.70	1.20E−1
 N,N′-Bis(2-hydroxyethyl)ethylenediamine	1.21	0.41	1.94E−1

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

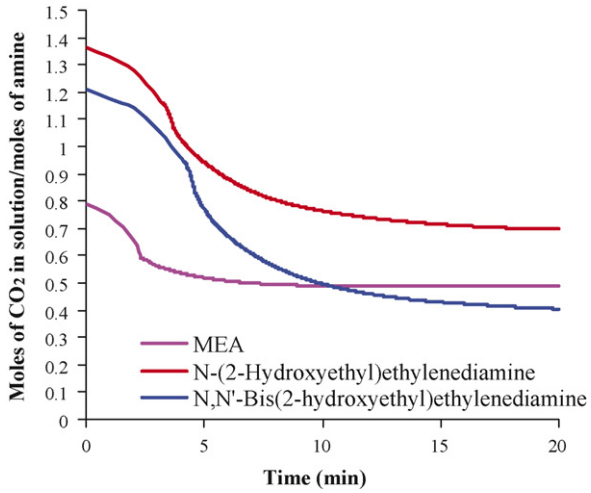


Fig. 16 – Influence of the number of OH group in aq. diamine-based absorbent for desorption of CO_2.

hydroxyethyl)ethylenediamine), which results in an increased amount of CO_2 released in desorption.

While comparing the effect of an increase in the number of different functional groups on their desorption capacity from Figs. 14 and 17, the absorbent with five amine groups present in structure is having the highest desorption capacity of around 75% whereas the absorbent with the two hydroxyl groups desorption capacity is close to 66%. Therefore from these results it can be noticed that an increase in number of amine groups and hydroxyl groups enhances the desorption capacity of CO_2 in amine-based absorbents.

3.6. *Effect of functional groups in cyclic amines*

Cyclic amines are known to be potential absorbents for CO_2 absorption due to their fast absorption rate and high

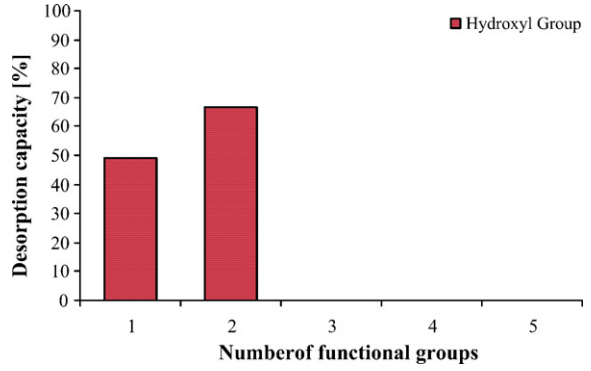


Fig. 17 – Influence of the number of amine groups in aq. amine-based absorbent for the desorption capacity (%) of CO_2 at pseudo-equilibrium.

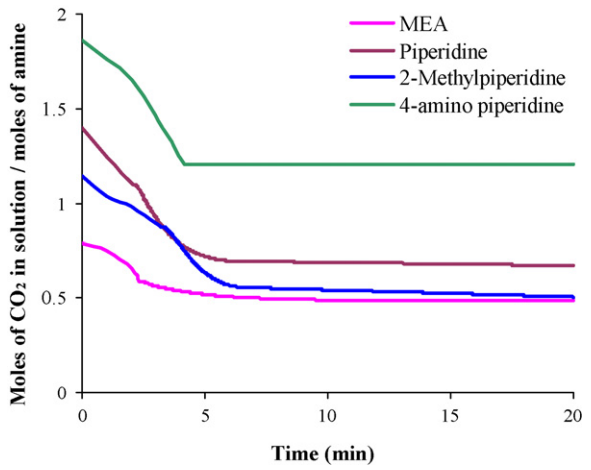
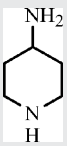
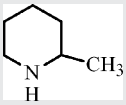


Fig. 18 – Influence of different functional group substitution on aq. saturated cyclic monoamines for desorption of CO_2.

absorption capacity. Therefore, the effect of different substituted saturated cyclic amine and diamine compounds was investigated. In Figs. 18 and 19(a and b) and Table 9 the comparison between saturated monoamine and similar compounds, substituted with an alkyl and amine groups is presented. It must be noticed that the concentration of piperidine and 2-methylpiperidine and 4-amino piperidine was kept to 0.5 moles/l. Results in Fig. 18 and Table 9 shows that initial desorption rate is increased with a substitution of an amine group at the saturated ring (4-amino piperidine). This could be caused by the effect that the amine group substitution at

Table 9 – Capacity of aq. saturated cyclic monoamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 Piperidine	1.40	0.67	4.57E−1
 2-Methylpiperidine	1.14	0.50	3.01E−1
 4-Aminopiperidine	1.90	1.20	7.39E−1

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

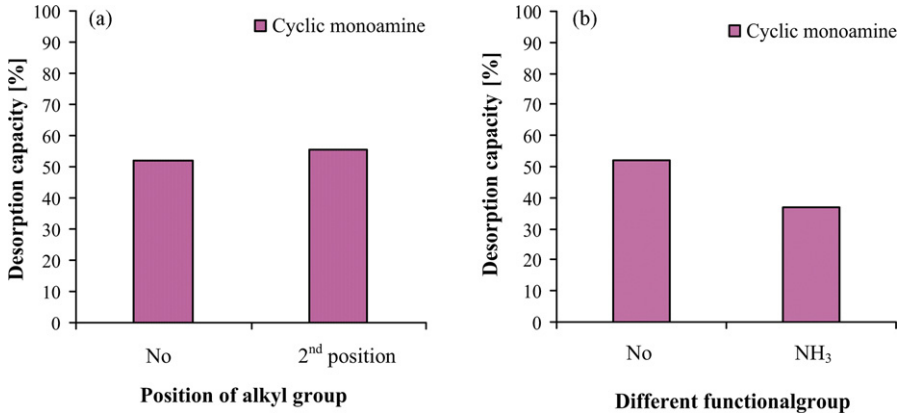


Fig. 19 – (a) Influence of alkyl group substitution in aq. saturated cyclic monoamine on desorption capacity (%) of CO_2 at pseudo-equilibrium. (b) Influence of amine group substitution in aq. saturated cyclic monoamine on desorption capacity (%) of CO_2 at pseudo-equilibrium.

the saturated cyclic ring increase the formation of carbonate in the solution and hence, results in faster initial desorption rate. Whereas, substitution of methyl groups at the second position in the saturated ring (2-methyl piperidine) results in a slight decrease in initial desorption rate.

Results from Figs. 18 and 19(a and b) show that the substitution of the methyl group at the second position in the saturated ring (2-methyl piperidine) slightly increases the desorption capacity up to 0.50 moles of CO_2/moles of amine (see Table 9), that is approximate 55% of CO_2 is desorbed.

Whereas substitution of an amine group by a side chain at the saturated ring (4-amino piperidine) decreases desorption capacity 1.20 moles of CO_2/moles of amine (see Table 9) that is 37% of CO_2 is desorbed.

In Figs. 20 and 21 and Table 10 the effect of a methyl group substitution on a saturated cyclic diamine is presented. It should be noticed that the concentration of piperazine, 1-methylpiperazine and *trans*-piperazine, 2,5-dimethyl was kept to be at 0.5 moles/l in these experiment. From Fig. 20, it can be noticed that initial desorption rate of *trans*-piperazine, 2,5-dimethyl is slightly higher than 1-methyl piperazine. This could be caused due to high electronegative effect imposed by two methyl groups on the saturated cyclic diamine. That can favour the accessibility of the lone-pair electrons of the amine group for CO_2. Hence, higher concentration of carbonate species was present in the system that cause faster CO_2 desorption. Still nonsubstituted cyclic diamine was noticed to have high initial desorption rate (see Table 10).

Results from Figs. 20 and 21 and Table 10 show that a substitution of one methyl group in the saturated ring at the 1st carbon position (1-methyl piperazine) decreases the desorption capacity up to 0.67 moles of CO_2/moles of amine that is approximate 43% of CO_2 is desorbed, when compared with two methyl group substitution on the second and fifth position in the saturated ring (*trans*-piperazine, 2,5-dimethyl) up to 0.59 moles of CO_2/moles of amine that is 56% of CO_2 is desorbed. It was also noticed that the nonsubstituted saturated amine (piperazine) has the highest desorption capacity compared to substituted saturated cyclic amine that reaches up to 0.40 moles of CO_2/moles of amine that is approximate 70% of CO_2 is desorbed.

The effect of different functional groups in cyclic diamine was also investigated. Figs. 22 and 23 and Table 11 shows the effect of substitution of amine, alkyl and hydroxyl group at the saturated cyclic diamine compound. It should be noticed that the concentration of *N*-ethylpiperazine, 2-(1-piperazinyl)ethylamine and 2-(1-piperazinyl)ethanolamine was 1 moles/l.

Results from Fig. 22 and Table 11 show that the substitution of the amine group in saturated cyclic diamine result in an increase in the initial desorption rate. Desorption loading of the saturated cyclic diamines substituted with an amine, alkyl

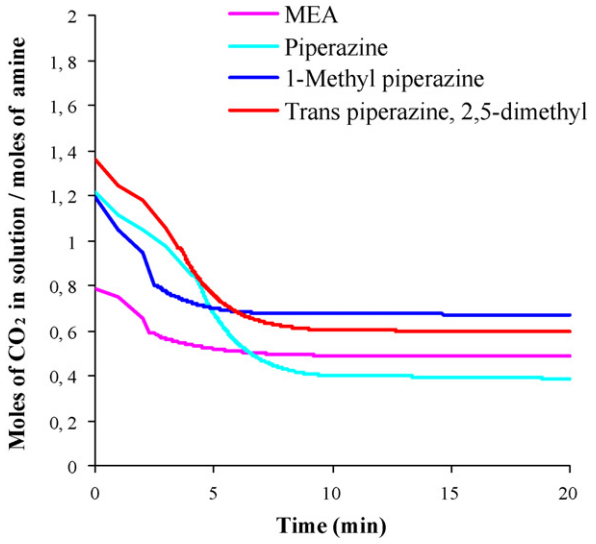


Fig. 20 – Influence of an alkyl group substitution on aq. saturated cyclic diamine-based absorbent for desorption of CO_2.

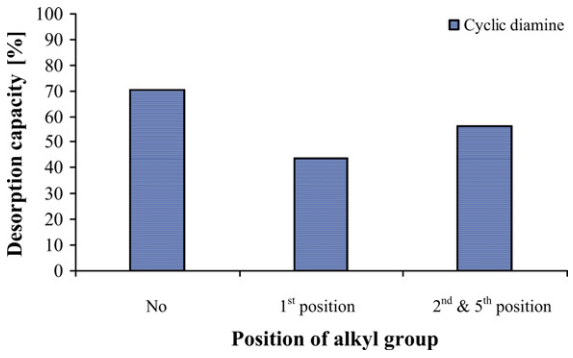
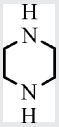
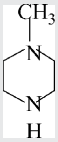
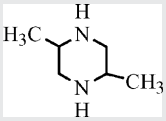


Fig. 21 – Influence of the position of alkyl group in aq. saturated cyclic diamine-based absorbent on desorption capacity (%) of CO_2 at pseudo-equilibrium.

Table 10 – Capacity of aq. saturated cyclic diamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 Piperazine	1.30	0.40	6.08E−2
 1-Methyl piperazine	1.19	0.67	1.30E−2
 *trans*-Piperazine, 2,5-dimethyl	1.36	0.59	4.08E−2

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

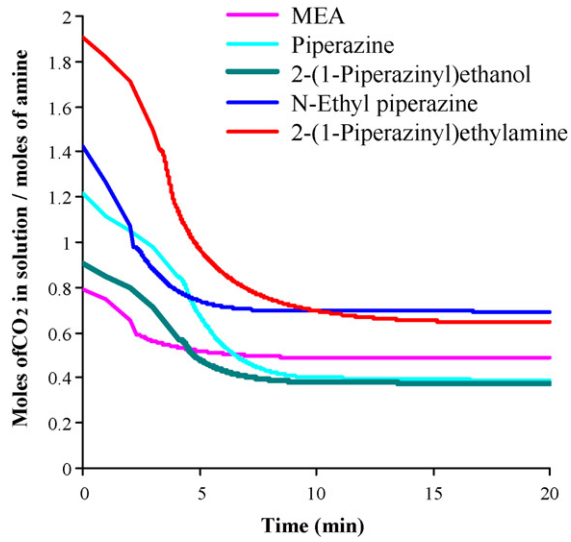


Fig. 22 – Influence of a side chain on aq. saturated cyclic diamine-based absorbent for desorption of CO_2.

or hydroxyl group were 0.69, 0.65 and 0.38 moles CO_2/moles amine, respectively (see Table 11). From these results it is clear that an amine group (2-(1-piperazinyl)ethylamine) and hydroxyl group (2-(1-piperazinyl)ethanol) substitution in saturated cyclic diamine result in somewhat higher desorption capacity of approximate 66 and 58% of CO_2 respectively when compared to alkyl group substituted saturated cyclic diamine (N-ethyl piperazine) in which only 51% of CO_2 is desorbed (see Fig. 23).

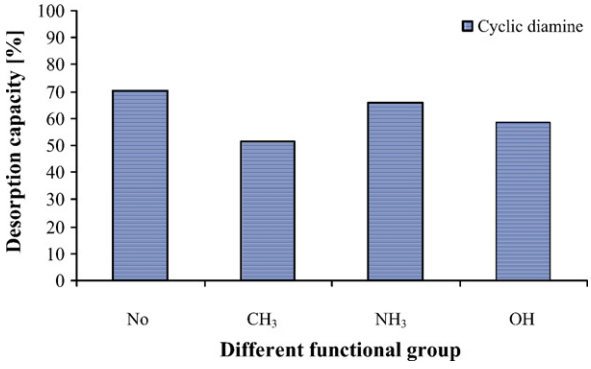
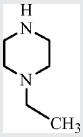
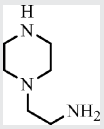
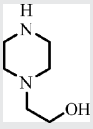


Fig. 23 – Influence of the different functional groups substitution on saturated cyclic diamine on desorption capacity (%) of CO_2 at pseudo-equilibrium.

Hence, from these results it is concluded that the amine group is a more suitable substituted functional group to enhance the initial desorption rate. Still nonsubstituted saturated diamines are having higher desorption capacities. Whereas, hydroxyl and alkyl group substitution results in a slight decrease in the initial desorption rate (see Table 11). Comparison could be made from the results for mono- and di-saturated cyclic amine and similar compounds substituted with different functional groups from Figs. 21 and 23. Results show that the nonsubstituted saturated diamine absorbent is having the highest desorption capacity.

Finally, the effect of different ring shapes was investigated. Figs. 24 and 25 and Table 12 show the results from azeti-

Table 11 – Capacity of aq. saturated cyclic diamine-based absorbents

Aqueous absorbent	CO_2 loading		
	A	B	C
 N-ethylpiperazine	1.43	0.69	5.01E−2
 2-(1-Piperazinyl)ethylamine	1.90	0.65	1.20E−1
 2-(1-Piperazinyl)ethanol	0.90	0.38	5.69E−2

Absorption: A (moles CO_2/moles amine); desorption: B (moles CO_2/moles amine); slope value of initial desorption rate: C (moles/m^3 s).

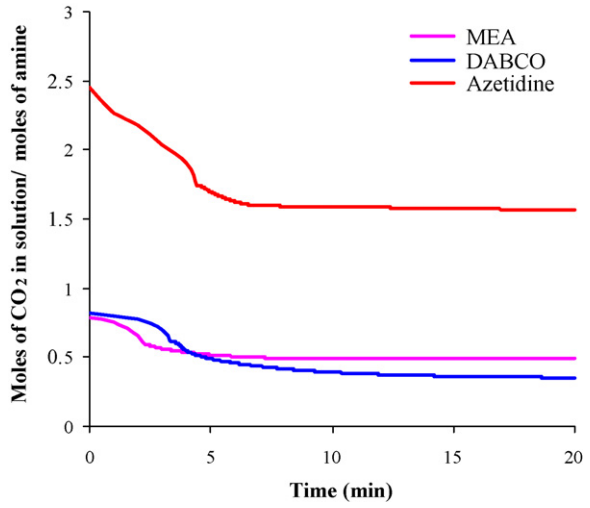


Fig. 24 – Comparison of various ring shape structure for desorption of CO_2 in aq. absorbents.

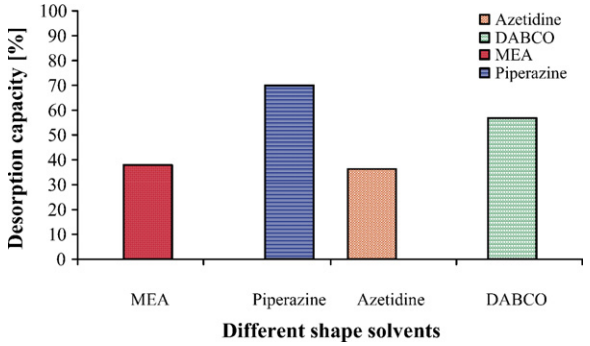
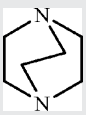


Fig. 25 – Comparison of various shape absorbent on desorption capacity (%) of CO_2 at pseudo-equilibrium.

dine and DABCO desorption. Concentration of azetidine and DABCO was kept to be 0.24 and 2.5 moles/l, respectively in these experiments. Fig. 24 shows that DABCO has a slightly higher initial desorption rate compared to azetidine (see Table 12).

Results from Fig. 25 and Table 12 show that DABCO is having higher desorption capacity reaches up to 0.35 moles CO_2/moles amine (see Table 12) that is 57% of CO_2 is desorbed. Whereas, in azetidine with small ring shape structure noticed to be having lower desorption capacity that is 36% of CO_2 is desorbed.

Table 12 – Capacity of various shape absorbent

Aqueous absorbent	CO_2 loading		
	A	B	C
 Azetidine	2.45	1.56	1.80E−2
 DABCO	0.83	0.35	5.95E−2
Or 1,4-Diazabicyclo [2.2.2] octane			

Absorption: *A* (moles CO_2/moles amine); desorption: *B* (moles CO_2/moles amine); slope value of initial desorption rate: *C* (moles/m^3 s).

4. Conclusion

The present study revealed some of the structural effects of various amine-based absorbent on their initial CO_2 desorption rate and desorption capacities at pseudo-equilibrium. For alkyl and diamine-based absorbents chain lengths of six carbon between amine and the functional group it is observed that may have high CO_2 desorption capacities. Whereas compounds with alkanolamines chain lengths of four carbons are having higher desorption capacities up to 49% of CO_2 is desorbed at pseudo-equilibrium. In alkyl and alkanolamine-based absorbents the initial desorption rate was found to be high for four carbon chain lengths. In diamine-based absorbents chain lengths with six carbon was noticed to show an increase in initial desorption rate. Alkyl group substitution at the α-carbon to the amine group results in an enhanced desorption capacity. This shows the effect of steric hinderance that enhances the desorption capacity. Substitution of different functional groups at the β-carbon to amine groups decreases the initial desorption rate. Increase in the amine group in the absorbent structure shows an increase in the desorption capacity, e.g. for five number of amine group desorption capacity reaches up to 70% of CO_2 is desorbed. It is also noticed that the increase in the number of amine groups up to four results in an increase in the initial desorption rate. The presence of two hydroxyl groups in the diamine-based absorbent shows an increase in desorption capacity up to 60% of CO_2 is desorbed at pseudo-equilibrium. Nonsubstituted saturated cyclic diamines showed higher desorption capacities of around 70% of CO_2 is desorbed compared to the substituted saturated cyclic diamine-based absorbent. In saturated cyclic monoamine the desorption capacities are slightly increased with the substitution of an alkyl group at the cyclic ring, it reaches up to 55% of CO_2 is desorbed. In both saturated cyclic mono- and di-amine-based absorbents amine group substitution with the side chain at the ring enhances the initial desorption rate. Hence, the results presented in this study could be an advantage in the development of an improved amine-based CO_2 absorbent, which will lead to a better approach for development of new technologies in the CO_2 capture area.

Acknowledgements

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